AD-A286 214

REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 18, 1994	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE

A Catalytic Method for the Conversion of Silanes to Stannanes

5. FUNDING NUMBERS

Grant #N00014-91-J-1043
R&T Code 3135014
Harold E. Guard, Program Officer

6. AUTHOR(S)

Benjamin P. Warner and Stephen L. Buchwald

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
Department of the Navy
Chemistry Division, ONR 331
800 North Quincy Street
Arlington, VA 22217-5660

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

Technical Report No. 5

94-35065

11. SUPPLEMENTARY NOTES

Prepared for Publication in the Journal of Organic Chemistry

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release and sale, distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The transformation of alkynyl-, allyl-, and benzyltrimethylsilanes to the corresponding tributylstannanes is reported. The reaction is initiated by the addition of tetrabutylammonium fluoride to a mixture of the silane and bis(tributyltin)oxide in tetrahydrofuran. The stannanes are isolated in ~quantitative yields after removal of the volatile bis(trimethylsilyl)oxide *in vacuo*.

14. SUBJECT TERMS silane, stannane, catalysis			15. NUMBER OF PAGES 9
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

94 11 14 011

OFFICE OF NAVAL RESEARCH

GRANT #N00014-91-J-1043

R&T Code 3135014
Harold E. Guard, Program Officer
Chemistry Division

Technical Report No. 5

A Catalytic Method for the Conversion of Silanes to Stannanes

by

Benjamin P. Warner and Stephen L. Buchwald

Prepared for Publication

in the

Journal of Organic Chemistry

Massachusetts Institute of Technology
Department of Chemistry
Cambridge, MA 02139

October 18, 1994

A Catalytic Method for the Conversion of Silanes to Stannanes

Benjamin P. Warner and Stephen L. Buchwald*

Department of Chemistry

Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

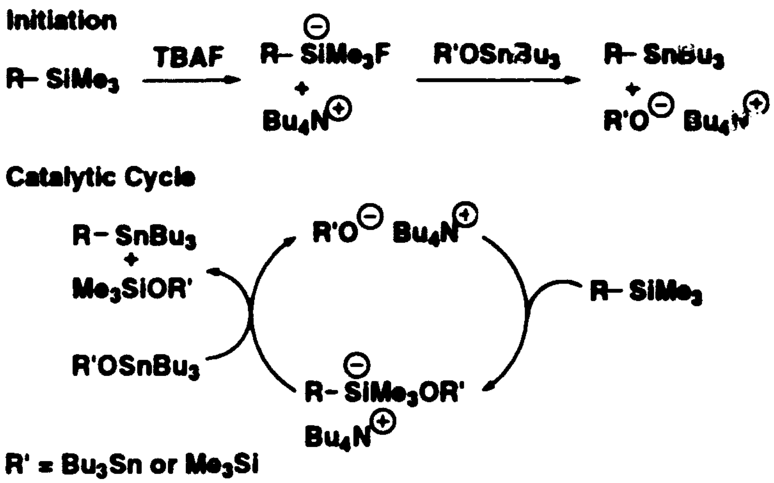
ABSTRACT

The transformation of alkynyl-, allyl-, and benzyltrimethylsilanes to the corresponding tributylstannanes is reported. The reaction is initiated by the addition of tetrabutylammonium fluoride to a mixture of the silane and bis(tributyltin)oxide in tetrahydrofuran. The stannanes are isolated in ~quantitative yields after removal of the volatile bis(trimethylsilyl)oxide *in vacuo*.

Revised

In the course of our studies of organo-main group compounds, we desired ready access to aryl(alkynyl)boranes. One of the most useful routes to such compounds was from the aryl(silyl)acetylenes generated by the palladium mediated coupling of an aryl [illegible]e and trimethylsilylacetylene.[1] The trimethylsilyl group would then be converted to a tributylstannyl group, and then to the corresponding alkynylborane.[2] Rather than the usual two step methods for converting alkynylsilanes to alkynylstannes,[3] we reasoned that the trimethylsilyl group could be removed under appropriate conditions, and the resulting anion would react with bis(tributyltin)oxide. This reaction would generate a new alkoxide, and the cycle would be repeated. We found that tetrabutylammonium fluoride (TBAF) is an excellent catalyst for the process, the presumed course of which is shown in Scheme

Scheme 1



We believe that this method for generating alkynylstannanes from silanes has advantages in terms of cost and ease of use. This reaction utilizes inexpensive bis(tributyltin)oxide rather than the more costly and moisture-sensitive tributyltin chloride.[5] The reaction allows the conversion of alkynylsilanes, as well as allyl- and benzyltrimethylsilane, to the corresponding tributylstannanes in one step, as opposed to desilylation and isolation of the terminal alkyne.[3] Finally, the product is isolated in

quantitative yield with removal of the volatile bis(trimethylsilyl)oxide the only purification needed.[6]

The reaction was carried out by first charging a sealable Schlenk tube with an appropriate silane (1 to 1.05[7] equiv), bis(tributyltin)oxide (0.5 equiv), and THF. A small amount of TBAF (0.02 equiv) was then added and the solution was heated at 60 °C for 2.5 h (16 h for allyl and benzyl silane), at which time the solvent and bis(trimethylsilyl)oxide are removed *in vacuo*. Allyl,[8] benzyl, and alkynylsilanes all react to generate the corresponding stannanes in excellent yields without further purification (Table 1).

[Table 1]

In summary, we have developed an efficient method for the conversion of alkynyl, benzyl, and allyl silanes to the corresponding stannanes.

Experimental Section:

General Considerations:

All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity-300, Varian XL-300, Varian XL 301, or Bruker AC-250 Fourier transform spectrometer. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 series Fourier transform spectrometer. Electron impact high resolution mass determinations (HRMS) were recorded on a Finnegan MAT System 8200. Elemental Analyses were performed by Desert Analytics; air sensitive samples were sent in sealed vials under nitrogen.

Tetrahydrofuran (THF) was dried and deoxygenated by refluxing and distilling from sodium / benzophenone ketyl under an argon atmosphere. All reagents, unless otherwise stated, are commercially available and were used as received. Yields refer to isolated yields of products of greater than 95% purity as estimated by ^{1}H NMR

spectrometry, and are an average of two or more separate experiments.

Representative Procedures: A flame dried sealable Schlenk flask under Argon was charged with **1a** (0.348 g, 2.0 mmol), and $(Bu_3Sn)_2O$ (0.596 g, 1.0 mmol), and THF (5 mL). TBAF (0.040 mL, 1 **M** in THF) was added, and the flask was sealed and stirred at 60 °C for 2.5 h, at which time the volatiles were removed *in vacuo* to yield **1b** as a colorless oil with no further purification necessary (0.764 g, 98 %).

Compounds **1a-4a**, **9a**, and **10a** were purchased from Aldrich Chemical Co., Inc. Compounds **5a-8a** were prepared according to the literature. The spectral data for **6a**,[9] **1b**,[10] and **2b**,[11] have been reported in the literature. Compounds **3b** and **9b** were compared with material purchased from Aldrich Chemical Co., Inc.

5a:[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.26 (s, 9H), 7.54 (d, *J* = 18.0 Hz, 2H), 7.57 (d, *J* = 18.0 Hz, 2H); IR (Film): alkyne 2158, nitrile 2234.

7a:[12] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.18 (s, 9H), 1.59 (m, 4H), 2.11 (m, 4H), 6.18 (m, 1H); IR (Film): alkyne 2146.

8a:[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.34 (s, 18H), 7.28 (dd, *J* = 5.7, 3.3 Hz, 2H), 7.51 (dd, *J* = 5.7, 3.3 Hz, 2H); IR (Film): alkyne 2161.

4b:[13] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.5 Hz, 9H), 1.00 (t, *J* = 8.3 Hz, 6H), 1.30 (m, 6H), 1.55 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 92.91, 83.94, 28.79, 26.97, 13.57, 11.36; IR (Film): alkyne 2036.

5b: ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (t, *J* = 7.3 Hz, 9H), 1.07 (t, *J* = 8.0 Hz, 6H), 1.36 (m, 6H), 1.6 (m, 6H), 7.51 (d, *J* = 8.2 Hz, 2 H), 7.53 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.2, 131.7, 128.7, 118.5, 110.5, 108.0, 99.9, 28.9, 27.0, 13.7, 11.3; IR (Film): nitrile 2363, alkyne 2228; HRMS: Calcd. for $C_{21}H_{31}NSn$: 417.1478. Found: 417.1476.

6b:[14] ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.5 Hz, 9H), 0.99 (t, *J* = 8.1 Hz, 6H), 1.32 (m, 6H), 1.53 (m, 6H), 3.37 (s, 3H), 4.09 (s, 2H); IR (Film): alkyne 2149.

7b:[15] ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.2 Hz, 9H), 0.98 (t, *J* = 8.1 Hz, 6H), 1.34 (m, 10H), 1.57 (m, 10H), 2.09 (m, 4H), 6.10 (m, 1H); IR (Film): alkyne 2126.

8b: ^1H NMR (300 MHz, $CDCl_3$): δ 0.92 (t, *J* = 7.2 Hz, 18H), 1.06 (t, *J* = 12 Hz, 12H), 1.36 (m, 12H), 1.6 (m, 12H), 7.17 (dd, *J* = 5.7, 3.4 Hz, 2 H), 7.42 (dd, *J* = 5.8, 3.4 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.6, 127.2, 126.3, 108.5, 97.4, 28.9, 27.0, 13.6, 11.2; IR (Film): alkyne 2135; Anal: Calcd. for: $C_{34}H_{58}Sn_2$: C, 57.99; H, 8.3. Found: C, 57.97; H, 8.58.

10b:[16] ^1H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, *J* = 7.8 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 9H), 1.28 (m, 6H), 1.4 (m, 6H), 2.3 (t, $J_{Sn\text{-}H}$ =27 Hz, 2H), 6.9 (m, 3 H), 7.16 (m,, 2 H).

Acknowledgment: This work was supported, in part, by the Office of Naval Research to whom we are grateful. SLB acknowledges additional support as a Camille & Henry Dreyfus Teacher-Scholar.

Supplementary material available: Copies of ^1H and ^{13}C NMR spectrum for **5b** (2 pages).

References:

1. Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis*, **1980**, 627.
2. Wrackmeyer, B.; Nöth, H. *Chem. Ber.* **1977**, *110*, 1086.
3. Cf. Williamson, B.L.; Tykwynski, R.R.; Stang, P.J. *J. Am. Chem. Soc.* **1994**, *116*, 93. and references therein.
4. Nakamura, E.; Kuwajima, I. *Angew. Chem. Int. Ed. Eng.* **1976**, *15*, 498.
5. Tributyltin chloride is $47.59/mole and bis(tributyltin)oxide is $33.65/mole of tributyltin from Aldrich Chemical Co., Inc. Prices are from the 1992-93 catalog, and are derived from the largest sized bottles listed.
6. We note that the stannanes generated can be used without purification or removal of

solvent and volatiles, in Stille reactions. For example, **1a** was converted to **1b**, then 1 equivalent of iodobenzene, 0.025 equivalents of palladium (II) acetate, and 0.05 equivalents of triphenylphosphine were added. After heating the reaction mixture to 60 °C for 14 h, followed by aqueous work up, and flash chromatography, diphenylacetylene was isolated in 81 % yield. Echavarren, A.M.; Stille, J.K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. Cummins, C.H. *Tetrahedron Lett.* **1994**, *35*, 857.

7. Solutions of TBAF contain 5% water, which protonates some of the silane or stannane. For alkynylstannanes, this reaction is reversible, but for allyl and benzyl trimethylsilane, a small amount of material was unavoidably lost.

8. Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043.

9. Labaudiniére, L.; Hanaizi, J.; Normant, J.F. *J. Org. Chem.* **1992**, *57*, 6903.

10. Loque, M.W.; Teng, K. *J. Org. Chem.* **1982**, *47*, 2549.

11. Keinan, E.; Peretz, M. *J. Org. Chem.* **1983**, *48*, 5302.

12. Stadnichuk, M.D.; Petrov, A.A. *Zh. Obschch. Khim.* **1961**, *31*, 411. [Chem. Abstr. **1961**, *55*, 23329a.]

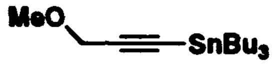
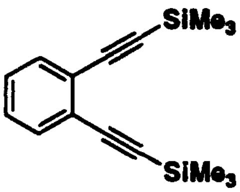
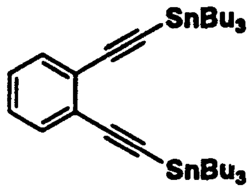
13. Hartmann, H.; Wagner, H.; Karbstein, B.; el A'ssar, M.K.; Reiss, W. *Naturwissenschaften*, **1964**, *51*, 215.

14. Zhai, D., Zhai, W.; Williams, R.M. *J. Am. Chem. Soc.* **1988**, *110*, 2501. Williamson, B.L.; Stang, P.J.; Arif, A.M. *J. Am. Chem. Soc.* **1993**, *115*, 2590.

15. Ito, Y.; Inouye, M.; Murakami, M. *Tetrahedron Lett.* **1988**, *29*, 5379.

16. Davies, A.G.; Roberts, B.P.; Smith, J.M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2221.

Table 1

	Substrate[a]		Product	Yield[c]
1a	Ph—≡—$SiMe_3$	1b	Ph—≡—$SnBu_3$	97%
2a	Me—≡—$SiMe_3$	2b	Me—≡—$SnBu_3$	98%
3a	Me_3Si—≡—$SiMe_3$	3b	Bu_3Sn—≡—$SnBu_3$	98%
4a	Me_3Si—≡—≡—$SiMe_3$	4b	Bu_3Sn—≡—≡—$SnBu_3$	98%
5a	*p*-NC-Ph—≡—$SiMe_3$	5b	*p*-NC-Ph—≡—$SnBu_3$	99%
6a		6b		98%
7a		7b		97%
8a		8b		99%
9a[b]		9b		95%
10a[b]		10b		95%

[a]Reaction run for 2.5 h except as noted.
[b]Reaction run for 16 h.
[c]Yields refer to isolated product of >95% purity as estimated by ^{1}H NMR.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (1)*
Chemistry Division, ONR 331
800 North Quincy Street
Arlington, Virginia 22217-5660

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5320

Dr. John Fischer, Director (1)
Chemistry Division, C0235
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Peter Seligman (1)
Naval Command, Control and
Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Richard W. Drisko (1)
Naval Facilities & Engineering
Service Center
Code L52
Port Hueneme, CA 93043

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

* Number of copies to forward